

REMARKS

Claims 27-28 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Ilardi et al. (U.S. Pat. No. 5,466,389) in view of Kern (Hand Book of Semiconductor Wafer Cleaning Technology) and further in view of Sehested et al. (J. Phys. Chem.). While the Office Action states that the Kern reference provides a general teaching that hydrogen peroxide is functionally equivalent to ozone, hydrogen peroxide is not equivalent to ozone in the current cleaning context as claimed. The applicants previously submitted a Declaration of Stefan DeGendt stating that hydrogen peroxide is not capable of removing organic photoresist contaminants from silicon substrates. As evidence, the applicants submitted with the Declaration of Stefan DeGendt an article by Werner Kern published in the Journal of the Electrochemical Society (1990), Vol. 137, pp. 1887-1892, in which Dr. Kern stated that hydrogen peroxide would not eliminate the organic photoresist contaminants. Thus, the same person who authored the reference upon which the Office Action relies as providing a teaching that hydrogen peroxide is equivalent to ozone states that, in fact, the two are not equivalent.

In addition, the applicants hereby submit the Supplemental Declaration of Stefan DeGendt pursuant to 37 C.F.R. §1.132, which was previously submitted in related application serial no. 09/022,834. In his Declaration Dr. DeGendt states that "hydrogen peroxide and ozone are not functionally equivalent when removing organic contaminants resulting from a previous lithographic step." Supplemental Declaration of Stefan DeGendt, ¶6. Dr. DeGendt provides experimental data in the form of a table, as shown in paragraph 8 of his supplemental declaration. In reviewing the data, Dr. DeGendt states:

As shown in the enclosed graph, the amount of resist removed using ozone is orders of magnitude greater than the amount of resist removed using hydrogen peroxide. As merely one example, the amount of resist removed for ozone at 50 ppm and hydrogen peroxide at 50 ppm is 169.8 nm to .1 nm, respectively. This is a difference of over three orders of magnitude. Thus, it is my conclusion that in the context of removing organic contaminants resulting from a previous lithographic step, hydrogen peroxide is not functionally equivalent to ozone.

Supplemental Declaration of Stefan DeGendt, ¶10. Thus, based on the cleaning ability of ozone, being orders of magnitude greater than hydrogen peroxide at removing the resist, Dr. DeGendt concludes that hydrogen peroxide is not equivalent to ozone. Therefore, the applicants respectfully

submit that the rejection based on the Ilardi in view of Kern and Sehested references is improper and should be withdrawn.

Claims 29-33 and 35 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Heyns et al. (New Wet Cleaning Strategies for Obtaining Highly Reliable Thin Oxide) in view of Ilardi et al. (U.S. Pat. No. 5,466,389) and Kern (Hand Book of Semiconductor Wafer Cleaning Technology) and further in view of Sehested et al. (J. Phys. Chem.). This rejection, like the rejection of claims 27-28 addressed above, relies on modifying the Ilardi reference in view of Kern to teach the use of ozone rather than hydrogen peroxide. However, as demonstrated above, application of the Kern reference is inappropriate here because ozone and hydrogen peroxide are not functionally equivalent when removing organic contaminants resulting from a previous lithographic step. Therefore, the applicants respectfully request withdrawal of this rejection as well.

As further evidence of the non-obviousness of the present claims, the applicants draw the Examiner's attention to the experiments disclosed on pages 23-25 of the present specification (entitled "Application 2"). These experiments present a comparative study of the cleaning efficiency of aqueous ozone with and without the scavenger acetic acid and are the sort of experiments described in MPEP § 716.02(a). Cleaning data are presented for un-implanted positive and negative resist wafers as well as for implanted positive resist wafers.

The reported data demonstrate that an aqueous ozone solution containing the scavenger acetic acid enhanced cleaning efficiency of implanted wafers by 50% relative to an aqueous ozone solution not containing acetic acid – 90 nm/min for an acetic acid-containing aqueous ozone solution compared to only 60 nm/min for an aqueous ozone solution without acetic acid. Page 24, ll. 22-24.

The specification also reports on p. 24, ll. 24-33 and depicts in figure 9 that the addition of the scavenger acetic acid to an aqueous ozone solution enhanced the cleaning efficiency of the solution by up to 50% on un-implanted negative resist wafers (1.2 nm/(min·ppm) for the acetic acid-containing ozone solution compared to only 0.8 nm/(min·ppm) for the aqueous ozone solution without acetic acid) and up to 88% on un-implanted positive resist wafers (8.5 nm/(min·ppm) for the acetic acid-containing ozone solution compared to only 4.5 nm/(min·ppm) for the aqueous ozone solution without acetic acid).

The applicants respectfully submit that the cited art does not teach or suggest that such a high degree of improvement in cleaning efficiency of a semiconductor surface by an aqueous ozone solution as observed by the applicants could be achieved by adding a scavenger to the solution. Consequently, on this basis alone the presently pending claims are not obvious over the cited art.

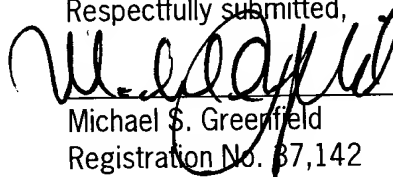
In view of the foregoing the applicants respectfully request reconsideration and withdrawal of all pending § 103 rejections.

The applicants acknowledge the provisional double patenting rejections and will take appropriate actions once the claims are in their final form and otherwise deemed allowable.

If there are any questions or comments regarding this Response or application, the Examiner is encouraged to contact the undersigned attorney as indicated below.

Date: October 16, 2003

Respectfully submitted,



Michael S. Greenfield
Registration No. 37,142

Telephone: 312-913-0001
Facsimile: 312-913-0002

McDonnell Boehnen Hulbert & Berghoff
300 South Wacker Drive
Chicago, IL 60606

The Evolution of Silicon Wafer Cleaning Technology

Werner Kern*

Lam Research Corporation, Advanced Research Center, San Diego, California 92126

ABSTRACT

The purity of wafer surfaces is an essential requisite for the successful fabrication of VLSI and ULSI silicon circuits. Wafer cleaning chemistry has remained essentially unchanged in the past 25 years and is based on hot alkaline and acidic hydrogen peroxide solutions, a process known as "RCA Standard Clean." This is still the primary method used in the industry. What has changed is its implementation with optimized equipment: from simple immersion to centrifugal spraying, megasonic techniques, and enclosed system processing that allow simultaneous removal of both contaminant films and particles. Improvements in wafer drying by use of isopropanol vapor or by "slow-pull" out of hot deionized water are being investigated. Several alternative cleaning methods are also being tested, including choline solutions, chemical vapor etching, and UV/ozone treatments. The evolution of silicon wafer cleaning processes and technology is traced and reviewed from the 1950s to August 1989.

The importance of clean substrate surfaces in the fabrication of semiconductor microelectronic devices has been recognized since the early days of the 1950s. As the requirements for increased device performance and reliability have become more stringent in the era of VLSI and ULSI silicon circuit technology, techniques to avoid contamination and processes to generate very clean wafer surfaces have become critically important. Besides, over 50% of yield losses in integrated circuit fabrication are generally accepted to be due to microcontamination. Trace impurities, such as sodium ions, metals, and particles, are especially detrimental if present on semiconductor surfaces during high-temperature processing (thermal oxidation, diffusion, epitaxial growth) because they may spread and diffuse into the semiconductor interior. Impurities must also be removed from surfaces before and/or after lower temperature steps, such as chemical vapor deposition, dopant implanting, and plasma reactions. Postcleaning after photoresist stripping is necessary for every mask level throughout the production process.

Many wafer cleaning techniques have been tested and several are being used. The generally most successful approach for silicon wafers without metallization uses wet-chemical treatments based on hydrogen peroxide chemistry. This process has remained essentially unchanged during the past 25 years, but important advances have been made in its technical implementation. The evolution of the cleaning technology for premetallized silicon wafers from its beginning to the present time will be traced in this paper.

Type, Origin, and Effects of Contaminants

Impurities on silicon wafer surfaces occur in essentially three forms: (i) contaminant films, (ii) discrete particles, and (iii) adsorbed gases that are of little practical consequence in wafer processing. Surface contaminant films and particles can be classified as molecular compounds, ionic materials, and atomic species. Molecular compounds are mostly particles or films of condensed organic vapors from lubricants, greases, photoresist, solvent residues, components from plastic storage containers, and metal oxides or hydroxides. Ionic materials comprise cations and anions, mostly from inorganic compounds that may be physically adsorbed or chemically bonded (chemisorbed), such as sodium ions, fluoride ions, and chlorine ions. Atomic or elemental species comprise metals, such as gold and copper, that may be electrochemically plated out on the silicon surface from HF-containing solutions, or they may consist of silicon particles or metal debris from equipment.

The sources of impurities are manifold. In the case of particles, which can be detected and measured much more easily than contaminant films, the major sources are equipment, chemicals, factory personnel, and production processes. For example, mechanical equipment, process operations, furnace tubes, film deposition systems, gas piping,

and liquid containers are especially serious sources, whereas materials, liquid and gaseous chemicals, and ambient air tend to cause less particle contamination; but all contribute significantly to the generation of contaminant films. Static charge built up on wafers and carriers is a powerful mechanism of particle deposition, but is often overlooked and not properly dealt with.

Molecular contaminant films on wafer surfaces can mask effective cleaning or rinsing, cause poor adhesion of deposited layers, and lead to harmful decomposition products. For example, organic films, if heated to high temperatures in a nonoxidizing atmosphere, can carbonize and form silicon carbide that can nucleate polycrystalline regions in an epitaxial deposit. Ionic films and metals cause a host of problems in semiconductor devices. During high-temperature processing or on application of an electric field they may diffuse into the bulk of the semiconductor structure or spread on the surface, leading to electrical defects, device degradation, and yield losses. For example, highly mobile alkali ions may cause drift currents and unstable surface potential, shifts in threshold and flatband voltages, surface current leakage, and may lower the oxide breakdown field of thermally grown layers. In the growth of epitaxial silicon layers, sufficiently high concentrations of ions can give rise to twinning dislocations, stacking faults, and other crystal defects. Atomic metals, especially the heavy metals, can affect minority-carrier lifetime, surface conduction, electrical device stability, and lead to structural defects in epitaxial layers. Particles may cause blocking in photolithography and etching or rinsing, and lead to shorts if they are conductive and located adjacent to conductor lines. They are considered potential killer defects if their size exceeds one tenth of the linewidth. Particles that are present during film growth or deposition may lead to pinholes, material voids, cracks, and the generation of defects noted above, depending on their chemical composition. Additional information on the nature, origin, detection, and effects of contaminants is available from selected papers and reviews (1-13).

Early Cleaning Procedures

During the early stages of silicon wafer processing until about 1970, one used organic solvent extraction, boiling nitric acid, aqua regia, concentrated hydrofluoric acid, and hot acid mixtures as cleaning chemicals. Mixtures of sulfuric acid-chromic acid led to chromium contamination and caused ecological problems of disposal. Mixtures of sulfuric acid and hydrogen peroxide caused sulfur contamination. Aqueous solutions containing hydrogen peroxide had long been used for cleaning electron tube components (14, 15) but not for semiconductors. In general, impurity levels and particles in process chemicals were high and in themselves tended to lead to surface contamination. Particulate impurities were removed by ultrasonic treatment in detergent solutions or by brush scrubbing. The first caused frequent wafer breakage and the second often deposited more debris from the brushes than it removed from the wafer surfaces.

* Electrochemical Society Active Member.

Cleaning Processes Based on Hydrogen Peroxide Solutions

Cleaning chemistry.—The first systematically developed cleaning process for bare or oxidized silicon wafers was based on a two-step oxidizing and complexing treatment with hydrogen peroxide solutions: (i) an alkaline mixture at high pH followed by (ii) an acidic mixture at low pH (1). The choice of chemicals was based on reaction chemistry, oxidation potentials, reagent purity, reagent volatility, safety, and economy. The process was developed at RCA, introduced to device production in 1965, and published in 1970 (1).

In the first treatment step the wafers are exposed to a hot mixture of water-diluted hydrogen peroxide and ammonium hydroxide. This procedure was designed to remove organic surface films by oxidative breakdown and dissolution to expose the silicon or oxide surface for concurrent or subsequent decontamination reactions. Group IB and IIB metals and several other metals, including gold, silver, copper, nickel, cadmium, zinc, cobalt, and chromium, are dissolved and removed by the complexing effectiveness of ammonium hydroxide; copper, for example, forms the $\text{Cu}(\text{NH}_3)_4^{+2}$ amino-complex.

The second treatment step exposes the rinsed wafer to a hot mixture of water-diluted hydrogen peroxide and hydrochloric acid. This procedure was designed to remove alkali ions, and cations such as Al^{+3} , Fe^{+3} , and Mg^{+2} , that form NH_4OH -insoluble hydroxides in basic solutions. This second step also eliminates metallic contaminants that were not entirely removed by the first treatment, such as gold. Electrochemical displacement replating of heavy metals from the solution is prevented by formation of soluble complexes with the dissolved metal ions.

Solution composition, process conditions, and effectiveness.—The solution compositions are based on ultrafiltered deionized water, electronic grade NH_4OH (29 weight percent (w/o) as NH_3), electronic-grade HCl (37 w/o), and high-purity "unstabilized" H_2O_2 (30%). The hydrogen peroxide must be low in aluminum and stabilizer additives (sodium phosphate, sodium stannate, or amino derivatives) to prevent wafer recontamination. The usual volume ratios for the solution used in the first treatment step are 5 H_2O_2 :1 H_2O :1 NH_4OH ; the mixture is known as "RCA standard clean 1 or SC-1." The usual volume ratios for the second solution are 6 H_2O_2 :1 H_2O :1 HCl . "RCA standard clean 2, or SC-2." Treatments by the original immersion technique are typically 10 min at 75°–80°C in each solution. Higher temperatures must be avoided to minimize excessive thermal decomposition of the hydrogen peroxide. Intermediate and final rinses in ultrafiltered deionized water are used.

The effectiveness of the process was demonstrated by sensitive radioactive tracer measurements with several radionuclides (1, 16) and by capacitance-voltage bias temperature measurements of MOS capacitors (1). H_2O_2 solutions are unstable at elevated temperature, especially at high pH, rapidly decomposing to H_2O and O_2 . The processing temperature should therefore be kept at 75°–80°C to sufficiently activate the mixtures without causing excessively fast decomposition.

Optional processing steps.—A preliminary clean-up treatment with a hot H_2SO_4 - H_2O_2 mixture (2:1 vol) can be used advantageously for grossly contaminated wafers having visible residues, such as photoresist layers. Another step, not noted in the original paper (1), concerns an etch in HF solution for bare silicon wafers. Since the hydrous oxide film from the SC-1 treatment may trap trace impurities, its removal before the SC-2 step should be beneficial. A 15s immersion in 1% HF- H_2O solution is sufficient to remove this film, as evidenced by the change from the hydrophilic oxidized surface to hydrophobic after stripping. However, unless high-purity and point-of-use ultrafiltered and particle-free HF solution is used under controlled conditions, more harm than good can result. A silicon surface that was exposed to HF is highly reactive and immediately attracts particles and organic contaminants from solutions, DI water, and the ambient air. Contrary to C-1, the

subsequent SC-2 solution, which has no surfactant activity, will not eliminate these contaminants. It may therefore be preferable to rely on the dissolution action of SC-1 that dissolves and regrows the hydrated oxide layer at about the same rate. If the pre-clean is used, then the 1% HF step prior to SC-1 is acceptable since SC-1 will remove the contaminants. Exposure of bare silicon wafer to HF after SC-2 should not be done since it would destroy the passivated surface resulting from SC-2 and cause recontamination.

Immersion technique.—The original RCA cleaning process was based on a simple immersion technique. Several different and improved techniques have been introduced over the years, as will be discussed. The immersion procedure is done in vessels of fused silica to prevent leaching of aluminum, boron, and alkalis if Pyrex glass is used. A batch of wafers is immersed in the SC-1 or SC-2 solution under the prescribed conditions. The reaction is terminated by overflow quenching with cold DI water before the wafers are transferred to a flow rinsing system with ultrafiltered DI water, followed by spin drying in a wafer centrifuge. Several types of refined wet bench immersion systems for automated processing are now available for large-scale production (17–19).

Centrifugal spray cleaning.—In 1975, Fill Corporation introduced the first centrifugal spray cleaning machine specifically designed for automatic operation with corrosive chemicals. The wafers rotate past a stationary spray column. Filtered acids and reagent solutions, including hot SC-1, SC-2, and DI water, are pressure-fed into a mixing manifold and then directed as a dispersed spray onto the spinning wafers. The spin-rinsed wafers are dried by high-speed spinning in heated nitrogen. A reduced volume of freshly mixed reagents is used and the process is faster than by immersion. The chemical cleaning efficiency, according to FSI, is comparable with that of immersion, but particles are removed more efficiently. Improved versions of this system (20) and other types of spray processing machines (17–19) are widely used but tend to require considerable maintenance.

Megasonic cleaning.—The original objective of the RCA cleaning process was the removal of contaminant films rather than particles. To complement this technique, the megasonic particle removal system was developed at RCA and first described in 1979 (21). A highly effective noncontact scrubbing action on both front and backside surfaces of the wafers is achieved by ultrahigh-frequency sonic energy while the wafers are submerged in the cleaning solution. The sonic waves of 850–900 kHz are generated by an array of piezoelectric transducers. Particles ranging in size from several micrometers down to about 0.3 μm can be efficiently removed with input power densities of 2–5 W/cm^2 . For comparison, ultrasonic systems operate typically at 20–80 kHz and require power densities of 1 p to 50 times that of the megasonic system but are much less effective for removing very small particles. Megasonic cleaning made it possible to remove simultaneously contaminant films and particles in one operation by combining the peroxide treatments with megasonics. The system allows removal of particles, organic contaminant films, and lightly adsorbed contaminants with diluted SC-1 solution at the ambient bath temperature of only 35°–42°C. Chemisorbed inorganics generally require higher temperatures (about 70°C) for complete desorption with SC-1 and SC-2, but no quantitative data are available as yet. A detailed paper on megasonic wafer cleaning was published in 1985 (22). Improved megasonic systems built under license from RCA have become available in the past few years from Vertec, Semiconductor Technology, and Esteek.

Closed system chemical cleaning.—A system termed Full-Flow™, developed in 1986 by CFM Technologies, Incorporated, is based on keeping the wafers stationary and enclosed in the system during the entire cleaning, rinsing, and drying process (23). The vessel containing the wafers is hydraulically controlled to remain filled with hot or cold process fluids, including SC-1 and SC-2, that flow sequentially and continuously over stationary wafers loaded in

cassettes. The repeated crossing through the gas/liquid phase boundaries in the immersion techniques is thereby eliminated. The system thus avoids recontamination problems encountered when wafers are pulled out from a liquid.

Chronological Literature Survey

Beginning in 1972, independent investigators examined and verified by various analytical methods the effectiveness of the RCA cleaning method published in 1970 (1). This section chronologically reviews references on silicon wafer cleaning pertaining specifically to hydrogen peroxide solutions, up to mid-1989.

In 1972 Henderson published results on the evaluation of SC-1/SC-2 cleaning, using high-energy electron diffraction and Auger electron spectroscopy as analytical methods (24). He concluded that the process is well-suited for wafer cleaning prior to high-temperature treatments, as long as quartz ware is used for processing, as specified by us (1). An additional final etch in HF solution after SC-1/SC-2 caused carbon contamination and surface roughening during vacuum heating at 1100°C due to loss of the protective 1.5 nm thick C-free oxide film remaining after SC-2. Maak et al. (1973) investigated the removal of inorganic contaminants, including Cu and heavy metals, from silica-sol polished wafers by several reagent solutions (25). Using Rutherford backscattering, they concluded that SC-1/SC-2 preoxidation cleaning removes all elements heavier than Cl. Sulfur and chlorine remained after either SC-1, SC-2, or other cleaning procedures at $10^{13}/\text{cm}^2$. SC-1/SC-2 cleaning eliminated Ca and Cu much more reliably than did HF-HNO₃. Amick (1976) reported the presence of Cl on Si after SC-2 and S after H₂SO₄-H₂O₂; he used spark source mass spectrometric analysis (26). In 1976 Kern and Deckert published a brief review of surface contamination and semiconductor cleaning as part of a book chapter on etching (3). Murarka et al. (1977) studied methods for oxidizing Si without generating stacking faults and concluded that SC-1/SC-2 prior to oxidation is essential for this purpose (27). Gluck (1978) discussed removal of gold from Si by a variety of solutions. The desorption efficiency of SC-1 was more effective than that for SC-2, but the recommended sequential treatment of SC-1 followed by SC-2 was found to be the most effective method at high gold surface concentrations ($10^{-4}/\text{cm}^2$ range) (28). Peters and Deckert (1979) investigated photoresist stripping by solvents, chemical agents, and plasma ashing. The SC-1 procedure was the only acceptable technique by which the residues could be removed completely (29). Burkman (1981) reported on desorption of gold with several reagent solutions by centrifugal spraying. SC-1 type solution was much more effective than H₂SO₄-H₂O₂, while a SC-2 type alone showed poor efficiency (20).

Phillips et al. (1983) applied SIMS (secondary ion mass spectroscopy) to determine the relative quantities of contaminants on Si. Cleaned wafers were purposely contaminated with gross quantities of numerous inorganic materials and then cleaned by immersion or spray techniques with various aggressive reagents including aqueous regia, hot fuming HNO₃, and H₂SO₄-H₂O₂. The lowest residual concentrations for most impurity elements were obtained by spray cleaning with H₂SO₄-H₂O₂ followed by the SC-1/HF/SC-2 type cleaning sequence (30). Goodman et al. (1983) demonstrated by minority-carrier diffusion-length measurements the effectiveness of SC-1/SC-2 for desorbing trace metals on Si (31). The author (1983) published a review of the subject on the occasion of the Citation Classic declaration of the original 1970-paper (32). In 1983 Watanabe et al. (33) reported dissolution rates of SiO₂ and Si₃N₄ films in SC-1. The rate of thermally grown SiO₂ in SC-1 during 20 min at 80°C was a constant 0.4 nm/min, a significant rate for structures with thin oxide layers. The etch rate of CVD Si₃N₄ was 0.2 nm/min under the same conditions. Measurements by the author in 1981 (and published in 1984), however, indicated much lower oxide dissolution rates under nearly identical conditions (34). Film thicknesses were measured by ellipsometry after each of four consecutive treatments in fresh 5:1:1 SC-1 at 85°C and totaled only 7.0 nm/80 min, or 0.09 nm/min. Under the same

conditions, 6:1:1 SC-2 showed no loss. Similar results averaging 0.13 nm/min were obtained with thermal SiO₂ films grown on lightly or heavily doped Si. Wafers from the same sets were used to determine the etch rates of exposed Si in SC-1 solutions with decreasingly lower H₂O₂ content. No etching or attack of Si occurred until the H₂O₂ was reduced by more than 75% (34).

Bansal (1984, 1985) reported extensive results in particle removal by spray cleaning from Si wafers with SC-1/SC-2, H₂SO₄-H₂O₂, and HF solution of various purity grades. He found the RCA cleaning solutions to be the most effective (35, 36). Schwartzman et al. (1985) described simultaneous removal of particles and contaminant films by megasonic cleaning with SC-1 solutions (22). Ishizaka and Shiraki (1986) showed that atomically clean Si surfaces for MBE can be prepared below 800°C in UHV by thermal desorption of a thin (0.5-0.8 nm), passivating oxide layer that protects from C contamination (37). It is formed in a series of wet oxidation (HNO₃, SC-1) and HF-stripping steps, terminating with an SC-2 type treatment. Wong and Klepner (1986) used XPS analysis to examine Si after wet chemical treatments. RCA cleaning without buffered HF stripping resulted in about 30% of the Si atoms in the top 1.0 nm being oxidized, whereas with a final BHF step less than one monolayer of suboxide coverage resulted (39). Grundner and Jacob (1986) conducted extensive studies of Si surfaces after treatment with SC-1/SC-2 or 5% HF solutions, using x-ray photoelectron and high-resolution electron energy loss spectroscopy. Oxidizing solutions produced hydrophilic surfaces, whereas HF solution led to hydrophobic surfaces consisting mainly of Si-H with some Si-CH₃ and Si-F (39). In 1986 Becker et al. (40) reported on decontamination by different reagent sequences. SIMS analysis was used to test for the removal of Na, K, Ca, Mg, Cr, Cu, Al, and particle impurities. The best cleaning sequence for metallics was H₂SO₄-H₂O₂/SC-1/HF/SC-2. Reversing the order of SC-1 and HF was most effective for particle removal and slightly less so for metal ions. Kawado et al. (1986) found by SIMS that Al on Si wafers originated from impure H₂O₂ used in SC-2. Very high concentrations resulted if Pyrex vessels were used in the processing instead of fused quartz (41). In 1986 McGillivray et al. (42) investigated effects of reagent contaminants on MOS capacitors. Low field breakdown was more prevalent if preoxidation cleaning with SC-2 was terminated with HF solution instead of omitting it. No other significant differences in electrical properties resulted from these two treatments.

Lampert (1987) examined growth and properties of oxide films on Si in various aqueous solutions, including SC-1 and SC-2 (43). Gould and Irene (1987) studied the influence of preoxidation cleaning on Si oxidation kinetics (44). They found significant rate variations depending on treatment (SC-1/SC-2/HF, SC-1, SC-2, HF, no clean). Ruzyllo (1987) reported on similar experiments and found that various preoxidation cleans seem to affect structure and/or composition of the subsequently grown oxide rather than the reactivity of the Si surface (45). Slusser and MacDowell (1987) found that sub-ppm levels of Al in H₂O₂ used for SC-1/SC-2 causes a substantial shift (up to 0.2V) in the flatband voltage of a dual dielectric. Aluminum concentrates on the wafer surface, and basic media such as SC-1, lead to 5 times higher levels than acid (SC-2) solutions (10). In 1987 Kern and Schnable reviewed wafer cleaning in a new chapter on wet etching (11). Probst et al. (1988) stated that for achieving predictable diffusion from implanted doped poly-Si into single-crystal Si, an SC-1/SC-2 treatment of the substrate prior to poly-Si deposition is imperative (46). Khilnani (1988) discussed various aspects of semiconductor cleaning, including the RCA process (12). Peterson (1988) showed that the sequencing of cleaning solutions (H₂SO₄-H₂O₂, SC-1, SC-2, HF) can have dramatic effects on particle levels (47). In 1989 Morota et al. (48) reported on the contamination of SC-1/SC-2 cleaned wafers by Na, K, Al, Cr, Fe, Ni, and Cu from solutions, showing that the absence or presence of an SiO₂ layer on the Si surface strongly affects adsorption. Desorption of Al and Fe was most effective with HF-H₂O, and that

of Cu and Cr with SC-2. The same authors (49) postulated that metals of high enthalpy of oxide formation adsorb on the oxidized Si surface by oxide formation, whereas metals of low ionization tendency deposit electrochemically on the bare Si. Gould and Irene (1989) studied the etching of native SiO_2 and Si in $\text{NH}_4\text{OH}-\text{H}_2\text{O}$, BHF, and SC-1 by ellipsometry. Severe Si surface roughness resulted from NH_4OH less with BHF, and none with SC-1 (50). Ohmi et al. (1989) compared particle removal efficiency of several cleaning solutions. They found that 5:1:1 SC-1 efficiently removes particles larger than $0.3 \mu\text{m}$, but increases those smaller than $0.5 \mu\text{m}$ ("haze") unless the NH_4OH ratio was decreased to one half or less, in which case both types of particles were reduced efficiently. However, no processing conditions and effects of low- NH_4OH SC-1 on removal of chemical contaminant films were mentioned (51). Menon et al. (1989) evaluated effects of solution chemistry (5:1:1, SC-1, DI water) and particle composition on megasonic cleaning efficiency at various power levels. They concluded that cleaning efficiency depends on several factors and that megasonics can provide wafer cleanliness levels not previously attainable (52).

Alternative Cleaning Techniques

General.—Many techniques for cleaning silicon wafers have been tried over the years with various degrees of success. Some techniques are useful only for specific applications or may introduce undesirable side effects. For example, glow discharge techniques (53) such as plasma etching, effectively strip photoresist films but leave inorganic contaminants and metals behind. Various types of sputter-etching (53) can cause surface damage. Some techniques remain restricted to certain applications, such as plasma treatments for preparing small-geometry devices for metallization (54), or wet-chemical etching of the silicon to remove entire surface layers by etch dissolution (3, 11). The following few techniques have been found viable and, in some cases, can be a desirable addition or alternative to the processes based on hydrogen peroxide solutions.

Brush scrubbing, fluid jet, and ultrasonic techniques.—The removal of large particles (e.g., after sawing and lapping operations) has been accomplished since the early days with wafer scrubbing machines that dislodge particles hydrodynamically with brushes made of a hydrophilic material (such as nylon) while DI water or isopropyl alcohol is applied to the surface (55). A thin layer of fluid must be retained between the brush and the wafers by careful mechanical adjustment to prevent surface scratching (52). While many contradictory claims have been made (56), if properly maintained, brush scrubbing can be very effective for removing particles larger than $1 \mu\text{m}$ from planar and preferably hydrophilic wafer surfaces.

High-pressure fluid jet cleaning consists of a high-velocity jet of liquid sweeping over the surface at pressures of up to 4000 psi (55, 56). The liquid can be DI water or organic solvents. The shear forces effectively dislodge submicron particles and penetrate into dense topography, but damage to the wafer can result with improperly adjusted pressure (18).

Ultrasonic techniques use sonic energy of 20 kHz and above to dislodge particles. High-intensity sound waves generate pressure fluctuations that result in cavitation bubbles which upon collapsing, release enough energy to dislodge and disperse particles but can also lead to wafer damage (56). Menon et al. have recently investigated various cleaning liquids for removing particles from wafers by ultrasonic and spray jet techniques (57). DI water was best for removing polymeric particles, while ethanol-acetone (1:1) was best (better than Freons) for inorganic particles. Cleaning efficiency decreased with decreasing particle size. A unique acoustical cleaning system utilizing 20 kHz frequency and only DI water as medium was introduced by Estek in 1986 (18) but has been abandoned.

Choline cleaning.—In contrast to the mechanical techniques for particle removal discussed in the previous section, choline cleaning is a chemical treatment that removes

particles and some contaminant films but at the same time appears to add certain contaminants to the surface. Choline, which is trimethyl-2-hydroxyethyl ammonium hydroxide, was first proposed by Asano et al. in 1976 (58) as a replacement for inorganic bases for etching and cleaning. It is a strong and corrosive base without alkali elements and etches silicon like other bases. A formulation of the chemical is available from Mallinckrodt under the tradename "Summa-Clean SC-15 M," which is a dilute choline solution containing a surfactant and methanol. Etching of Si can be prevented by adding H_2O_2 as an oxidant (59). There is very little published information on this subject, most data being contained in proprietary technical reports with contradictory results. Polyflow engineering manufactures an automatic dual-chamber spray machine that uses a warm choline- H_2O_2 - H_2O mixture and a DI water spray rinse (18). In some procedures, the mixture replaces only SC-1 in the RCA cleaning procedure. In 1989 Kaos discussed oxide defect densities as a function of various preoxidation cleans including choline- H_2O_2 - H_2O , HF- H_2O , RCA cleans, and UV-ozone (60).

UV-ozone and other dry-cleaning techniques.—Irradiating a surface with short-wavelength UV from a mercury quartz lamp in the presence of oxygen is a powerful technique for removing many contaminants. Oxygen absorbs 185 nm radiation forming very active ozone and atomic oxygen (61). The technique is most suitable for oxidative removal of adsorbed organics, but is generally not effective for most inorganics or metals. Therefore, its use in the past has been limited, in general, to special applications, such as GaAs wafer cleaning. Improvements in oxide qualities have been attained by applying the technique after SC-1/SC-2/HF- H_2O , immediately before oxidation (62). Ruzyllo et al. (1989) have shown that UV- O_3 cleaning can replace SC-1 for removing organics (63), and Kaos reported improvements in properties of thermal oxide films (60).

Hoening (1988) investigated the use of dry ice snow for removing particles from wafers (64). Clean, liquid CO_2 from a tank is allowed to expand to form dry ice snow, which is blown across the surface. The sliding snow is quite effective for mechanically removing particles. Particle detachment by electrostatic techniques has been investigated but found to be impractical (12). In 1987 FSI Corporation introduced a processing system for anhydrous SF_6 gas phase etching of oxide and silicate films at room temperature (65). Applications to device processing were published in 1988 (66, 67). The contamination problems inherent with HF- H_2O solutions were avoided and in combination with the UV-ozone technique constitutes part of an ultrapure, integrated dry cleaning process that can be carried out entirely in the gas phase and may replace conventional wet techniques. Removal of metallic impurities could be accomplished by use of a remote microwave plasma (68), by chlorine radical techniques (67) or by photoinduced desorption in reactant gases (69). These new processes being developed are all designed to remove contaminants at low temperatures as volatile compounds without damaging the surface.

Wafer Rinsing and Drying

The last steps in wafer cleaning are rinsing and drying; both are extremely critical because clean wafers become recontaminated very easily if not processed properly. Rinsing after wet cleaning is done with flowing high-purity and ultrafiltered high-resistivity DI water, usually at room temperature (34). Megasonic rinsing is advantageous (52). Centrifugal spray rinsing (20) and rinsing in a closed system (23) have the advantage that the wafers are not removed between cleaning, rinsing, and drying. Wafer drying after rinsing must be done by physical removal of the water rather than by allowing it to evaporate. Spin drying accomplishes this and has been the most widely used technique. Hot forced-air drying is a preferred technique with less chance for particle recontamination (21, 22). Capillary drying is based on capillary action and surface tension to remove the water. Individual wafers are pulled out of DI water at $80-85^\circ\text{C}$; less than 1% of the water remains and evap rates, leaving a particle-free surface (71). In solvent

vapor drying wet wafers are moved into the hot vapor of a high-purity solvent, usually IPA (isopropyl alcohol), which displaces the water. The wafers dry quickly and are particle-free when the cassette is withdrawn above the hot vapor zone. Commercial drying systems for IPA and for nonflammable solvent mixtures are available (23, 70). The purity of the solvent is extremely important, and the water content during processing must be closely controlled, preferably by continuous recycling (51, 70).

Conclusion

Processes and techniques for cleaning, rinsing, and drying bare and oxide-coated silicon wafers have been reviewed from the 1950s to the present. Wet chemical cleaning based on hydrogen peroxide solutions and implemented by several techniques is still the main process used in industry. However, new wafer surface preparation technologies based on dry processing in the gas or vapor phase are being developed that promise superior results.

A great deal of research activity is taking place in this important area of technology, as evidenced by the scheduled presentation of over 40 papers (not referenced herein) at the First International Symposium on Wafer Cleaning Technology in Semiconductor Device Manufacturing, October 16-18, 1989, at the Electrochemical Society Fall Meeting.

Manuscript submitted Sept. 5, 1989; revised manuscript received Dec. 21, 1989. This was Paper 381 presented at the Hollywood, FL, Meeting of the Society, Oct. 16-18, 1989.

Lam Research Corporation assisted in meeting the publication costs of this article.

REFERENCES

- W. Kern and D. Puotinen, *RCA Rev.*, **31**, 187 (1970).
- W. Kern, *ibid.*, **31**, 207 (1970).
- W. Kern and C. A. Deckert, in "Thin Film Processes," J. L. Vossen and W. Kern, Editors, Chap. V-1, p. 411, Academic Press, New York (1978).
- P. F. Schmidt and C. W. Pierce, *This Journal*, **128**, 630 (1981).
- W. T. Stacy, D. F. Allison, and T. C. Wu, in "Semiconductor Silicon 1981," PV 81-5, H. R. Huff, R. J. Kriegler, and Y. Takeishi, Editors, p. 344, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1981).
- K. M. Eisele and E. Klausmann, *Solid State Technol.*, **27**, (10), 177 (1984).
- A. Licciardello, O. Puglisi, and S. Pignataro, *Appl. Phys. Lett.*, **49**, 41 (1986).
- J. Ruzyllo, *Technical Proc., Semicon/Europe '86*, p. 10, Zurich, March 8-9, 1986.
- J. R. Monkowski, in "Treatise on Clean Surface Technology," Vol. 1, K. L. Mittal, Editor, Chap. 6, p. 123, Plenum Press, New York (1987).
- G. J. Slusser and L. MacDowell, *J. Vac. Sci. Technol.*, **A5**, 1649 (1987).
- W. Kern and G. L. Schnable, in "The Chemistry of the Semiconductor Industry," S. J. Moss and A. Ledwith, Editors, Chap. 11, pp. 235 and 242-243, Chapman and Hall, New York (1987).
- A. Khilnani, in "Particles on Surfaces I: Detection, Adhesion, and Removal," K. L. Mittal, Editor, pp. 17-35, Plenum Press, New York (1988).
- D. C. Burkman, C. A. Peterson, L. A. Zazzera, and R. J. Kopp, *Microcontam.*, **6** (11), 57-68 and 107-111 (1988).
- D. E. Koontz, C. O. Thomas, W. H. Craft, and I. Amron, Symposium on Cleaning of Electronic Device Components and Materials, ASTM STP No. 245, p. 136 (1959).
- D. O. Feder and D. E. Koontz, *ibid.*, p. 40.
- W. Kern, *RCA Rev.*, **31**, 234 (1970).
- "Wafer Cleaning Equipment, 1986 Master Buying Guide," *Semicond. Int.*, **8** (13), 76 (1986).
- K. Skidmore, *ibid.*, **9** (8), 80 (1987).
- P. H. Singer, *ibid.*, **11** (8), 42 (1988).
- D. Burkman, *ibid.*, **4** (7), 103 (1981).
- A. Mayer and S. Schwartzman, *J. Electron. Mater.*, **8**, 885 (1979).
- S. Schwartzman, A. Mayer, and W. Kern, *RCA Rev.*, **46**, 81 (1985).
- A. E. Walter and C. F. McConnell, "Stationary In Situ Wet Chemical Processing: The Impact on Wafer Surface Phenomena," 1988 Microcontamination Conference, Santa Clara, CA; for a summary of this paper see *Semicond. Int.*, **12** (1), 36 (1989).
- R. C. Henderson, *This Journal*, **119**, 772 (1972).
- R. L. Meek, T. M. Buck, and C. F. Gibbon, *ibid.*, **120**, 1241 (1973).
- J. A. Arnick, *Solid State Technol.*, **47** (11), 47 (1976).
- S. P. Murarka, H. J. Levinstein, R. B. Marcus, and R. S. Wagner, *J. Appl. Phys.*, **48**, 4001 (1979).
- R. M. Gluck, Abstract 238, p. 640, The Electrochemical Society Extended Abstracts, Vol. 78-2, Pittsburgh, PA, Oct. 15-20, 1988.
- D. A. Peters and C. A. Deckert, *This Journal*, **126**, 883 (1979).
- B. F. Phillips, D. C. Burkman, W. R. Schmidt, and C. A. Peterson, *J. Vac. Sci. Technol.*, **A1**, 646 (1983).
- A. M. Goodman, L. A. Goodman, and H. F. Gossenberger, *RCA Rev.*, **44**, 328 (1983).
- W. Kern, *RCA Engineer*, **22**, 99 (July/August 1983).
- M. Watanabe, M. Harazono, Y. Hiratsuka, and T. Edamura, Abstract 130, p. 221, The Electrochemical Society Extended Abstracts, Vol. 83-1, San Francisco, CA, May 6-13, 1983.
- W. Kern, *Semicond. Int.*, **7** (4), 94 (1984).
- I. K. Bansal, *Microcontam.*, **2** (4), 35 (1984).
- I. K. Bansal, *Solid State Technol.*, **29** (7), 75 (1986).
- A. Ishizaka and Y. Shiraki, *This Journal*, **133**, 666 (1986).
- C. Y. Wong and S. P. Klepner, *Appl. Phys. Lett.*, **48**, 1229 (1986).
- M. Grundner and H. Jacob, *Appl. Phys.*, **A-39**, 73 (1986).
- D. S. Becker, W. R. Schmidt, C. A. Peterson, and D. Burkman, in "Microelectronics Processing: Inorganic Materials Characterization," ACS Symposium Series No. 296, L. A. Casper, Editor, Chap. 23, p. 368, American Chemical Society, Washington, DC (1986).
- S. Kawado, T. Tanigaki, and T. Maruyama, in "Semiconductor Silicon 1986," PV 86-4, H. R. Huff, T. Abe, and B. Kolbesen, Editor, p. 989, The Electrochemical Society, Softbound Proceedings Series, Pennington, NJ (1986).
- I. G. McGilivray, J. M. Robertson, and A. J. Walton, *ibid.*, p. 999.
- I. Lampert, Abstract 262, p. 381, The Electrochemical Society Extended Abstracts, Vol. 87-1, Philadelphia, PA, May 10-18, 1987.
- G. Gould and E. A. Irene, *This Journal*, **174**, 1031 (1987).
- J. Ruzyllo, *ibid.*, p. 1889.
- V. Probst, H. J. Bohm, H. Schaber, H. Oppolzer, and I. Weitzel, *ibid.*, **135**, 671 (1988).
- C. A. Peterson, in "Particles on Surfaces I: Detection, Adhesion, and Removal," K. L. Mittal, Editor, p. 37, Plenum Press, New York (1988).
- E. Morota, T. Yoshimi, and Y. Shimanuki, Abstract 237, p. 352, The Electrochemical Society Extended Abstracts, Vol. 89-1, Los Angeles, CA, May 7-12, 1989.
- T. Yoshimi, E. Morota, and Y. Shimanuki, *ibid.*, Abstract 238, p. 354.
- G. Gould and E. A. Irene, *This Journal*, **126**, 1108 (1989).
- T. Ohmi, H. Mishima, T. Mizuniwa, and M. Abe, *Microcontam.*, **7** (5), 25, 108 (1988).
- V. B. Menon, A. C. Clayton, and R. P. Donovan, *ibid.*, **7** (6), 81 and 107 (1989).
- J. L. Vossen, *J. Phys. E: Scientific Instrum.*, **12**, 159 (1979).
- J. L. Vossen, J. H. Thomas III, J.-S. Maa, and J. J. O'Neill, *J. Vac. Sci. Technol.*, **A-2**, 213 (1984).
- P. S. Burggraaf, *Semicond. Int.*, **4** (8), 71 (1981).
- J. Bardina, in "Particles on Surfaces I: Detection, Adhesion, and Removal," K. L. Mittal, Editor, p. 229, Plenum Press, New York (1988).
- V. B. Menon, L. D. Michaels, R. P. Donovan, and D. S. Ensor, *Solid State Technol.*, **32** (3), S7-S12 (1989).
- M. Asano, T. Cho, and H. Murarka, Abstract 354, p. 911, The Electrochemical Society Extended Abstracts, Vol. 78-2, Las Vegas, NV, Oct. 17-22, 1978.
- H. Murarka, K. J. Kurosawa, H. Hiratsuka, and T. Usami, Abstract 238, p. 570, The Electrochemical Society Extended Abstracts, Vol. 81-2, Denver, CO, Oct. 11-18, 1981.
- P. Burggraaf, *Semicond. Int.*, **11** (8), 15 (1989) (this is a summary of work reported by D.-B. Kao et al.).
- J. R. Vig, in "Treatise on Clean Surface Technology,"

- Vol. 1, K. L. Mittal, Editor, Chap. 1, Plenum Press, New York (1987).
62. J. Ruzyllo, G. T. Duranko, and A. M. Hoff, *This Journal*, 124, 2052 (1987).
 63. (a) J. Ruzyllo, A. M. Hoff, D. C. Frystak, and S. D. Hosain, *ibid.*, 136, 1474 (1989); (b) S. Baunack and A. Zehe, *Phys. Status Solidi A*, 115, 223 (1989).
 64. S. A. Hoening, in "Particles on Surfaces 1: Detection, Adhesion, and Removal," K. L. Mittal, Editor, p. 3.

- Plenum Press, New York (1988).
65. R. Cleavelin and G. Duranko, *Semicond. Int.*, 10 (12), 84 (1987).
 66. R. E. Novak, *Solid State Technol.*, 31 (3), 39 (1988).
 67. N. Miki, H. Kikuyama, M. Maeno, J. Morota, and T. Ohmi, 1988 IEDM Tech. Dig., 730.
 68. J. Ruzyllo, *Microcontam.*, 3 (3), 39 (1988).
 69. S. R. Palmer, *Rex Develop.*, 31 (5) 74 (1989).
 70. K. Skidmore, *Semicond. Int.*, 12 (8) 86 (1989).

Growth and Properties of LPCVD Titanium Nitride as a Diffusion Barrier for Silicon Device Technology

A. Sherman*

Varian Associates, Incorporated, Varian Research Center, Palo Alto, California 94303

ABSTRACT

Chemical vapor deposition has been used to deposit titanium nitride (TiN) on silicon wafers at low pressures in a cold-wall single-wafer reactor. Experiments are reported for pressures in the range of 100-300 mtorr and temperatures between 450°-700°C, with titanium tetrachloride and ammonia as reactants. Both hydrogen and nitrogen are evaluated as diluents. Deposition rates as high as 1000 Å/min have been achieved. The chemical nature of the films are evaluated by Auger and RBS techniques, while the morphology is depicted by SEM. For the most part, the films are stoichiometric and contain small quantities of oxygen, chlorine, and hydrogen. Film resistivities as low as 50 μΩ-cm are reported. Behavior of the TiN film as a diffusion barrier between silicon (boron doped) and aluminum, at annealing temperatures up to 550°C, is evaluated by measurements of contact resistance and diode leakage.

Coating of various metals with titanium nitride has been possible since the discovery in the 1930s of a chemical vapor deposition technique using electrically heated wires exposed to $\text{TiCl}_4 + \text{N}_2 + \text{H}_2$ gas mixtures (1, 2). In spite of the high temperatures required (>1000°C), commercial applications for jewelry coating (3) (gold color) and tool coating (4) (wear resistance) have seen considerable success. With the advent of reactive physical vapor deposition techniques (5-8), where a discharge in nitrogen is created with titanium atoms either evaporated or sputtered from one electrode, low temperature depositions (<500°C) became possible and applications of TiN coatings have become even more widespread. Other applications have been as a transparent heat mirror for architectural windows (9, 10), and as a high temperature diffusion barrier for silicon solar cells (11, 12).

Of particular interest, in the present paper, is the application of thin TiN films to silicon device technology. Because of the concern about exposure of circuits to high temperature processes, barrier films deposited by physical vapor techniques such as low temperature reactive sputtering (13-22) have been employed. However, as integrated circuit feature sizes shrink to submicron dimensions, the ability of physical techniques to uniformly coat high aspect ratio vias has become a concern. Accordingly, there has been an interest in developing a low temperature CVD process for deposition of thin films of TiN. One approach has been to explore plasma-enhanced CVD (PECVD) using TiCl_4 plus either nitrogen (23-26) or ammonia (27, 28). Another has been to investigate the low temperature thermal CVD process possible using $\text{TiCl}_4 + \text{NH}_3$, where depositions are possible at temperatures as low as 450°C. One recent investigation has focused on a low pressure CVD process (LPCVD) where many wafers are coated at one time in a hot wall tube reactor (29). Two others describe a LPCVD process in a cold-wall single-wafer reactor (30, 31). In this paper we elaborate on the latter approach.

Experimental

The titanium nitride depositions were carried out in a single-wafer cold-wall experimental reactor shown schematically in Fig. 1 (30). The chamber was stainless steel and enclosed a water and air-cooled lamp assembly used to heat the wafer. A single 10 kW tungsten halogen lamp

was employed that can heat a 4 in. wafer to 700°C rapidly. A load lock was used to maintain an oxygen and water vapor-free deposition environment.

Reactive gases were introduced through a showerhead gas distributor several inches above the wafer. The TiCl_4 and NH_3 were introduced through two separate lines and mixed for the first time in the shower head. As long as these two gases are mixed close to the hot wafer on which the deposit is to be made, the formation of NH_4Cl can be avoided as has been demonstrated in another experiment similar to this one (31).

Before beginning TiCl_4 or NH_3 flows, a nitrogen flow was established in the TiCl_4 line downstream of the TiCl_4 bottle. Next the TiCl_4 flow was initiated and after it was stabilized then the NH_3 flow was introduced. This procedure kept TiCl_4 and NH_3 from mixing in the TiCl_4 line and causing solid deposits there.

All of the gases were introduced through mass flow controllers (MFCs), including the TiCl_4 vapor which was obtained by heating TiCl_4 liquid to 40°C. The TiCl_4 line was heated to 50°C to prevent any condensation of this vapor. Since the pressure of the TiCl_4 vapor at 40°C was only 1 torr, we calibrated our Unit MFC (UFC-100) by measuring the time it took for a specified nitrogen mass flow (supplied at 40 torr) to increase the pressure in our chamber from 100 to 200 mtorr. We then repeated this measurement when the nitrogen was supplied at 10 psi. By this method

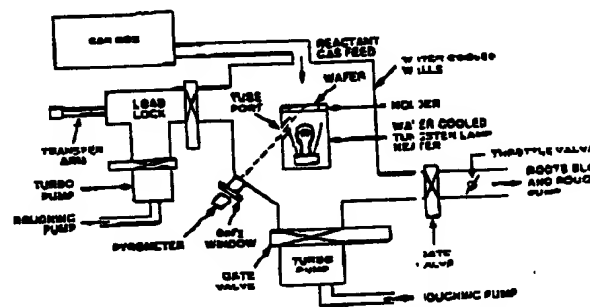


Fig. 1. Schematic of CVD reactor system

* Electrochemical Society Active Member.